university of groningen

University Medical Center Groningen

University of Groningen

Growth front roughening of room-temperature deposited oligomer films

Tsamouras, D.; Palasantzas, G.; de Hosson, J. T. M.

Published in:
Applied Physics Letters

DOI:
10.1063/1.1404132

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2001

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Tsamouras, D., Palasantzas, G., & de Hosson, J. T. M. (2001). Growth front roughening of room-temperature deposited oligomer films. *Applied Physics Letters*, *79*(12), 1801 - 1803. https://doi.org/10.1063/1.1404132

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 05-05-2023

Growth front roughening of room-temperature deposited oligomer films

D. Tsamouras
Department of Polymer Chemistry, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

G. Palasantzas and J. Th. M. De Hosson[a)]
Department of Applied Physics, Materials Science Center and the Netherlands Institute for Metals Research, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 19 March 2001; accepted for publication 26 July 2001)

Growth front scaling aspects are investigated by atomic force microscopy for oligomer 2,5-di-*n*-octyloxy-1,4-bis(4′-(styryl)styryl)-benzene thin films vapor deposited onto silicon substrates at room temperature. Analyses of the height–height correlation function for film thickness that are commonly used in optoelectronic devices, i.e., ranging between 15 and 300 nm, yield roughness Hurst exponents around $H=0.45\pm0.04$. Further, the root-mean-square roughness amplitude σ evolves with film thickness as a power law $\sigma\propto d^{\beta}$, with $\beta=0.28\pm0.05$. The nonGaussian height distribution and the measured scaling exponents (H and β) suggest a roughening mechanism close to that described by the Kardar–Parisi–Zhang [Phys. Rev. Lett. **56**, 889 (1986)] scenario indicating nonlinear film growth. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1404132]

Thin films grown under nonequilibrium conditions show, in many cases, scaling behaviors which are of technological interest in relation to physical properties.[1–5] Recently, there has been strong interest in organic thin films, either polymers or oligomers, as the active layer in molecular devices such as light-emitting diodes, solar cells, and field-effect transistors.[2,6] In particular, the transport phenomena are known to be strongly correlated to the electronic structure and self-organized order in the molecular assembly. Injection, transport, and recombination of charge carriers depend among other parameters on molecular packing, range of grain boundaries, and roughness of the formed interfaces.[7–9] Therefore, control of the film morphology is of primary concern for the optimization of electro-optical properties in organic-based photonic devices.[6]

So far, only scant research has been concentrated on growth properties of organic thin films.[3–5] These studies have shown that the root-mean-square (rms) roughness amplitude σ evolves with film thickness as a power law $\sigma\propto d^{\beta}$ with β the growth exponent in the range $0.25<\beta<1$, and a roughness exponent H in the range $H>0.6$.[3–5] The latter quantifies the degree of surface irregularity at short length scales ($<\xi$ with ξ the in-plane correlation length). For plasma polymer films,[3] the scaling exponents $0.9<H\leqslant1$ and $0.6<\beta\leqslant1$ were measured. The roughness evolution of a 100 nm thick T6 (sexithienyl) oligomer film,[4] with increasing substrate temperature (25 °C–250 °C) during deposition, was associated with a decreasing roughness exponent from $H=1.1$ to $H=0.7$. Finally, the growth of vapor deposited-polymerized linear poly(*p*-xylene) films[5] revealed the scaling exponents $H\approx0.7$, $\beta\approx0.25$, and $1/z=0.31$ ($\xi\sim d^{1/z}$) which were consistent with a roughening model due to monomer bulk diffusion.[5]

In this work, we will investigate scaling aspects of the growth front of the oligomer van der Waals thin films[6] grown by vapor deposition onto SiO_2 substrates held at room temperature (*RT*). The five-ring oligomer 2,5 -di-*n*-octyloxy-1,4-bis[4′-(styryl)styryl]-benzene is synthesized from solution, and its molecule exhibits a characteristic length of 2.9 nm [Fig. 1(a)].[10] During vacuum deposition, the molecules sublime at ~230 °C, and then as a whole unit condense on the Si wafer held at RT (ensured by proper water cooling). The base pressure in the deposition chamber was

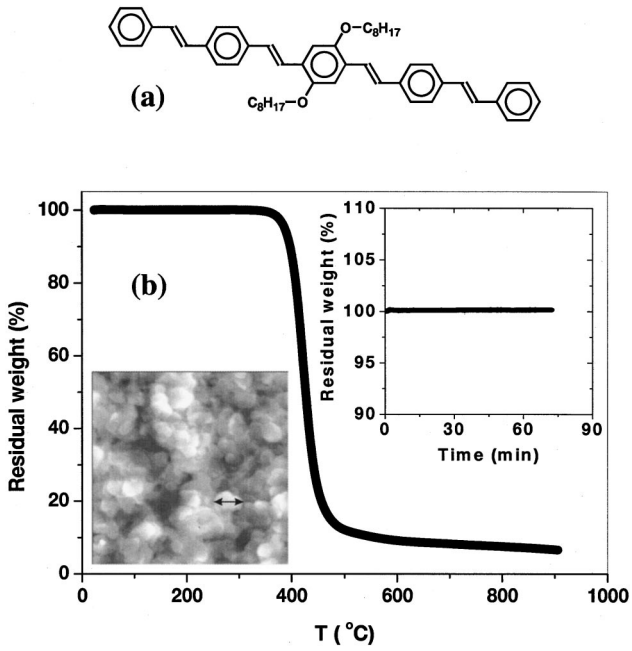

FIG. 1. (a) Chemical structure of the Ooct-OPV5 and (b) TGA for an Ooct-OPV5 specimen are shown. The upper inset shows an isothermal for the temperature (230 °C) and the heating time (< 45 min) used in our experiments. The lower inset shows a small scan size (800 nm) AFM topography image for a film grown at RT of thickness $d=105$ nm.

a)Author to whom all correspondence should be addressed; electronic mail: hossonj@phys.rug.nl

 © 2001 American Institute of Physics
Downloaded 06 Oct 2006 to 129.125.25.39. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

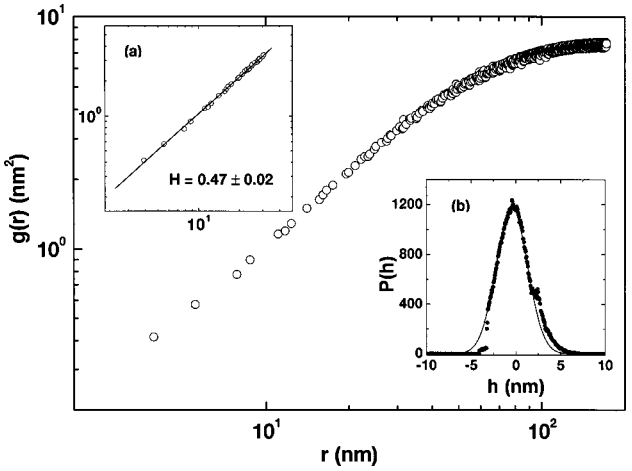

FIG. 2. Height–height difference correlation function $g(r)$ vs the in-plane distance r [scan size L to calculate $g(r)$ is $L=2000\,\text{nm}\gg\xi$] is shown. The rms roughness amplitude is $\sigma=1.90$ nm. The estimated correlation length is $\xi=76.2$ nm which compares with the cluster sizes in Fig. 1 (double arrow). (a) Linear fit at small length yields the roughness exponent $H=0.47\pm0.02$ and (b) Height distribution function are shown.

$\sim10^{-8}$ mbar, while during deposition it was typically $\sim10^{-7}$ mbar. During deposition, the average growth rate of $\approx$7.1 nm/min was monitored using a quartz crystal microbalance. Thermogravimetric analysis measurements (TGA)[11] showed that the molecule remains stable for temperatures up to $\sim$350 °C [Fig. 1(b), upper inset]. An additional isothermal scan for the temperature and the heating time used for the deposition of the thickest films in our experiments verifies the latter. After TGA analysis, the color of the samples remained unchanged. Therefore, molecule fragmentation can be excluded during evaporation.

The film surface morphology was measured using an atomic force microscope (AFM) (Digital Instruments Nanoscope IIIa) in tapping mode[12] to avoid any damage of the film surface [Fig. 1(b), lower inset]. The radius of the Si tip is $\leqslant$10 nm, and the side angle $\leqslant$10°, and 512×512 pixels were used during AFM imaging. Moreover, AFM analysis yielded a substrate roughness amplitude of about 0.3 nm, which is much smaller than that of the film surfaces. For each film thickness, the height–difference correlation function $g(r)=\langle[h(r)-h(\mathbf{0})]^2\rangle$ data from five AFM topography images (acquired at different locations on the film surface) were averaged (Fig. 2). $h(\mathbf{r})$ is the surface height at lateral position $\mathbf{r}[=(x,y)]$ on the surface relative to the mean surface height. The notation $\langle...\rangle$ means an ensemble average as well as an average of all possible choices of the origin. The self-affine scaling hypothesis requires that $g(r)=\text{Ar}^{2H}$ for $r\ll\xi$ and $g(r)=2\sigma^2$ for $r\gg\xi$ (with $A\sim\sigma/\xi^H$ a constant).[13] As the roughness exponent H decreases, the surface becomes more irregular (jagged) at length scales $r\ll\xi$.[1] The saturation regime of $g(r)$ yields σ, and the log–log plot at short length scales yields the roughness exponent H [Fig. 2(a)]. The correlation length ξ is given by $\xi=(2\sigma^2/A)^{1/2H}$ (intersection of power law and saturation lines). Since $\xi\gg2.9$ nm (molecule length), significant lateral correlation develop during growth. The calculation of $g(r)$ requires the use of a scan size at least ten times larger than the significantly large cluster sizes seen in the AFM images in order to capture all of the necessary lateral roughness wavelengths.[14]

The height distribution $P(h)$ shows deviations from the best Gaussian fit especially in the negative tail [left-hand side arrow in Fig. 2(b)]. To further quantify this point, we calculated the Skewness $S=\int h^3[P(h)/\int P(h)dh]dh/\sigma^3$, which is a measure of the distribution symmetry around a reference surface level. For Gaussian distribution $S=0$, while in the present case, we obtain $S=0.23(>0)$. Also for other film thickness, we obtain $S>0$ indicating violation of the $h\rightarrow-h$ symmetry and thus the presence of a nonlinearity associated with growth dependence on the local surface inclination.[17]

From Fig. 2, the roughness exponent H is in the range $H=0.45\pm0.04$ for the thickness range $15\,\text{nm}\leqslant d\leqslant300$ nm. These roughness exponents H are well below of any prediction of surface diffusion relaxation mechanism ($0.66\leqslant H\leqslant1$).[15,16] On the other hand, the Kardar–Parisi–Zhang (KPZ) type of growth,[17] where the dominant relaxation mechanisms are desorption or vacancy formation, lead to roughness exponent $H\approx0.4$.[1,18] Indeed, due to finite tip size effects, the actual roughness exponent could be closer to the KPZ value $H\approx0.4$.[19] The nonlinear term $(\nabla h)^2$ in the KPZ model [$\partial h/\partial t=v\nabla^2h+b(\nabla h)^2+n$ with "n" random Gaussian due to deposition and the term $v\nabla^2h$ associated with the surface relaxation][18] arises from the $h\rightarrow-h$ symmetry breaking, leading to growth dependence on surface inclination. By itself, the nonlinear term would convert a surface consisting of rounded hills into a surface of plateaus separated by narrow, step-sided canyons.[1] Such an effect appears to be consistent with the AFM topology images, as in Fig. 2, where the formation of fine nanosize [$\leqslant$100 nm; Fig. 1(b)] domains (plateaus) orientated almost randomly out of plane (with respect to the substrate) occurs, being separated by deeper groove networks that develop especially for thicker films.

Although, roughness exponents $H\leqslant0.3$ have been measured also on T6 oligomer films,[20] these studies did not address any further growth aspects such as the development of out-of-plane correlations as quantified by the growth exponent β.[20] Indeed, measurement of the exponent β ($\sigma\propto d^\beta$; Fig. 3 upper inset) yields $\beta=0.28\pm0.05$ which is within the predictions of the KPZ scenario $\beta\approx0.25$ (for $2+1$ dimensional growth).[1,18] We should point out, however, that with increasing film thickness a groove network develops. Since surface diffusion is excluded as the relaxation mechanisms of deposited molecules, the formation of column-like structures tens of nanometers in diameter with poor crystallinity which are separated by voids or are amorphous can occur.[21] The groove network might be responsible for the limited development of lateral correlation (Fig. 3; lower inset), leading to a slow increment of the correlation length ξ with increasing film thickness. At earlier stages of growth ($d\leqslant100\,\text{nm}$), a closely power law increment of the correlation length appears to develop with a corresponding dynamic exponent $1/z\approx0.31\pm0.05$ (as the fit to the first four data points indicates, Fig. 3 lower inset) which is smaller than the KPZ prediction $1/z\approx0.61$.[1,18]

In conclusion, the growth front roughening of vapor-deposited oligomer thin films (Ooct-OPV5) onto silicon-oxide substrates at room temperature appears to follow a scaling behavior close to the KPZ scenario. This is supported

Downloaded 06 Oct 2006 to 129.125.25.39. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

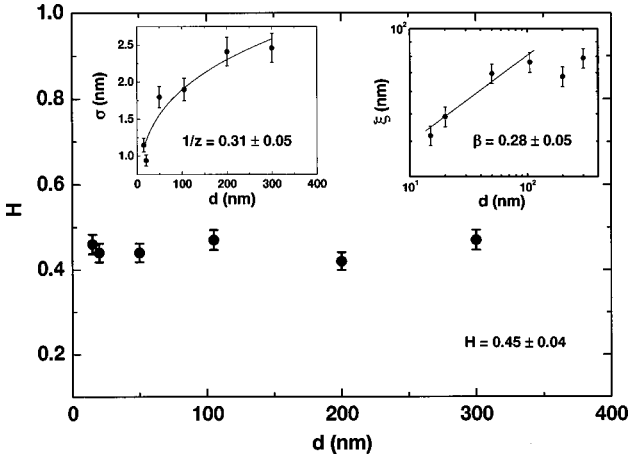

FIG. 3. Roughness exponent H vs film thickness are shown. An average value is estimated to be $H=0.45\pm0.04$. The inset on the left-hand side shows σ vs the film thickness d which grows with an exponent $\beta=0.28\pm0.05$ as the fit yields. The inset on the right-hand side shows the in-plane roughness correlation length ξ vs the film thickness d. The line depicts a linear fit for the first four data points to determine the dynamic exponent z.

by the roughness exponents $H=0.45\pm0.04$, the growth exponent $\beta=0.28\pm0.05$, as well as by the breakdown of the $h\rightarrow -h$ symmetry at the height distribution during growth. Further studies are in progress, in particular concentrating on the effect of substrate temperature on film surface morphology and the influence of the latter on electrical transport properties.[22]

The authors thank J. Wildeman for the synthesis of OoctOPV5 and G. A. van Ekenstein for TGA analyses. They also thank Dr. Y. P. Zhao, Professor M. Kardar, and Professor T. Halpin-Healy for stimulating comments on this work. This research has also been partly supported by a Marie Curie Individual Fellowship of the European Community program Human Potential for one of the authors (D.T.) under Contract No. HPMF-CT-199900010.

[1] P. Meakin, *Fractals, Scaling, and Growth Far from Equilibrium* (Cambridge University Press, Cambridge, UK, 1998); J. Krim and G. Palasantzas, Int. J. Mod. Phys. B **9**, 599 (1995); A. -L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, UK, 1995).
[2] *Polymers for Electronic and Photonic Applications*, edited by C. P. Wong (Academic, Boston, 1993); T.-M. Lu and J. A. Moore, Mater. Res. Bull. **20**, 28 (1997).
[3] G. W. Collins, S. A. Letts, E. M. Fearon, R. L. McEachern, and T. P. Bernat, Phys. Rev. Lett. **73**, 708 (1994).
[4] F. Biscarini, P. Samorí, O. Greco, and R. Zamboni, Phys. Rev. Lett. **78**, 2389 (1997); F. Biscarini, R. Zamboni, P. Samori, P. Ostoja, and C. Taliani, Phys. Rev. B **52**, 14868 (1995).
[5] Y. P. Zhao, J. B. Fortin, G. Bonvallet, G.-C. Wang, and T.-M. Lu, Phys. Rev. Lett. **85**, 3229 (2000).
[6] P. F. van Hutten, V. V. Krasnikov, and G. Hadziioannou, Acc. Chem. Res. **32**, 257 (1999).
[7] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. Spiering, R. A. J. Janssen, P. Herwig, and D. M. de Leeuw, Nature (London) **401**, 685 (1999).
[8] *Semiconducting Polymers: Chemistry, Physics and Engineering*, edited by G. Hadziioannou and P. F. van Hutten (Wiley, Weinheim, 2000).
[9] H. J. Brouwer, V. V. Krasnikov, T. A. Pham, R. E. Gill, P. F. van Hutten, and G. Hadziioannou, Chem. Phys. **65**, 227 (1998).
[10] R. E. Gill, A. Meetsma, and G. Hadziioannou, Adv. Mater. **8**, 212 (1996).
[11] For the technique of TGA, see A. Blaezek, *Thermal Analysis* (Van Nostrand Reinhold, London, 1972); B. Dickens and J. H. Flynn, in *Polymer Characterization: Spectroscopic, Chromatographic, and Physical Instrumental Methods*, edited by C. D. Craver (American Chemical Society, Washington DC, 1983).
[12] D. Sarid, *Scanning Force Microscopy with Applications to Electric, Magnetic and Atomic Forces*, revised edition (Oxford University Press, New York, 1994).
[13] G. Palasantzas, Phys. Rev. E **56**, 1254 (1997).
[14] G. Palasantzas and J. Krim, Phys. Rev. Lett. **73**, 3564 (1994).
[15] W. E. Wolf and J. Villain, Europhys. Lett. **13**, 389 (1990).
[16] Z.-W. Lai and S. Das Sarma, Phys. Rev. Lett. **66**, 2348 (1991).
[17] M. Kardar, G. Parisi, and Y. C. Zhang, Phys. Rev. Lett. **56**, 889 (1986); For skewed distribution aspects in Directed Polymer Problems in Random Media related to KPZ growth, see also T. Halpin-Healy, Phys. Rep. **254**, 215 (1995).
[18] M. Forest and L.-H. Tang, Phys. Rev. Lett. **64**, 1405 (1991).
[19] J. Aue and J. T. M. De Hosson, Appl. Phys. Lett. **71**, 1347 (1997).
[20] F. Biscarini, P. Samori, A. Lauria, P. Ostoja, R. Zamboni, C. Taliani, P. Viville, R. Lazzaroni, and J. L. Bredas, Thin Solid Films **284**, 439 (1996).
[21] D. L. Smith, *Thin-Film Deposition-Principles and Practice* (McGraw–Hill, New York, 1995).
[22] G. Palasantzas, Z. P. Zhao, G.-C. Wang, T.-M. Lu, J. Barnas, and J. T. M. De Hosson, Phys. Rev. B **61**, 11109 (2000).

Downloaded 06 Oct 2006 to 129.125.25.39. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp